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# Spectroscopic Studies on s-Tetrazine

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SPECTROSCOPIC STUDIES ON S- TETRAZINE

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SPECTROSCOPIC STUDIES ON s-TETRAZINE

by

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## ABSTRACT

From earlier studies it was shown that neither a vibronic analysis nor a normal coordinate vibrational analysis of s-tetrazine could be done until two low lying, fundamental, vibrational modes ($A_u$ and $B_{1u}$) were found. This work reports on the discovery of these two modes, the assignments of various infrared absorption peaks based on them, and the problems surrounding their observation. They are located at 337 $cm^{-1}$ and 252 $cm^{-1}$ respectively. Since s-tetrazine had previously been reported to be metastable at room temperature, it was desirable to study its decomposition. Both thermal and photochemical decomposition work is reported and discussed. The extinction coefficients in various portions of the visible and ultraviolet regions have been determined, and observations concerning a possible second $n \rightarrow \pi^*$ electronic transition are reported.

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TABLE OF SYMBOLS AND ABBREVIATIONS

| Symbol | Meaning |
|---|---|
| A | Angstroms |
| $A_g$, $B_{1u}$, etc. | Symmetry Species of Vibrational Modes |
| Br | Bromine Atom |
| C | Carbon Atom |
| C | Degrees Celcius (meaning will always be clear and distinct from usage as carbon atom) |
| Cl | Chlorine Atom |
| cm | Centimeters |
| $cm^{-1}$ | Wavenumbers or frequency (reciprocal centimeters) |
| Cs | Cesium Atom |
| $D_{2h}$ | Point Group of a particular symmetry |
| $\epsilon$ | Extinction Coefficient |
| EtOH | Ethyl Alcohol |
| F | Fluorine Atom |
| H | Hydrogen Atom |
| I | Iodine Atom |
| IR | Infrared |
| K | Potassium Atom |
| l | Liters |
| Li | Lithium Atom |
| mm | Millimeters |
| mm of Hg | Pressure in millimeters of mercury |
| mu | Millimicrons (Nanometers) |
| N | Nitrogen Atom |
| n | Electron in Nonbonding Orbital |
| NIR | Near Infrared |

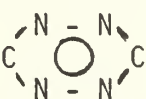| Symbol | Meaning |
| --- | --- |
| O | Oxygen Atom |
| P | Characteristic Lines in IR Spectra |
| $\pi$ | Electron in Bonding Pi Orbital |
| $\pi^*$ | Electron in Antibonding Pi Orbital |
| Q | Characteristic Line in IR Spectra |
| R | Characteristic Lines in IR Spectra |
| S | Sulfur Atom |
| u | Microns |
| UV | Ultraviolet |
| VIS | Visible |

# ACKNOWLEDGEMENTS
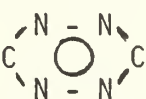
The author wishes to take this opportunity to express his sincere thanks and appreciation to Professor Glenn H. Spencer, his thesis advisor, who directed this research; to Professor John W. Schultz for his valuable assistance; and to LCDR Charles D. Kimble who worked closely with us and who furnished extremely helpful information.

Particular attention is also due to Professor Gilbert F. Kinney and the entire Department of Chemistry, most all of whom have helped in one way or another with this research.

# 1. INTRODUCTION

## 1.1 The s-Tetrazine Molecule

This thesis is concerned with spectrographic studies on symmetrical-tetrazine, an aromatic, six membered ring molecule which is isoelectronic with benzene and the other azines. It contains four nitrogen atoms in the ring,

H - C (N - N) C - H, with N-N bonds of 1.32 A length, C-N bonds of 1.33 A length, C-N-N bond angles of 116 degrees, and N-C-N bond angles of 127 degrees (1). It has $D_{2h}$ symmetry and is planar in the ground electronic state. Numbering of the atoms in the ring begins with a nitrogen atom and continues around the ring so as to have the minimum numbers assigned to the nitrogen atoms, hence it is sometimes referred to as 1,2,4,5 s-tetrazine.

Sublimation occurs at about 99 C and it exists as a brilliant red crystal below this sublimation point. It was reported to be meta-stable at temperatures up through its sublimation temperature (6). The vapor of s-tetrazine is red and shows a series of very sharp absorption bands in its visible spectrum. This series of bands is believed to be associated with the excitation of one of the lone pair, nonbonding electrons on a nitrogen atom to an antibonding pi molecular orbital (1,2,3), an $n \rightarrow \pi^*$ transition.

## 1.2 The Problem

Spencer, Cross, and Wiberg (1) attempted a complete vibronic analysis of s-tetrazine from a high resolution, visible spectra along with a series of infrared spectra. However, only a partial analysis could be made for two reasons. The Raman spectra could not be

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obtained.  This was due to the intense coloration of the solution and the resulting strong absorption of any Raman bands by the other s-tetrazine molecules in the solution.  The second difficulty was that they could not obtain two low lying, fundamental, infrared active, vibrational frequencies.  Specifically, these were the $A_u$ mode and a $B_{1u}$ mode.  [A comment on notation should be made at this point.  This thesis will use capital letters for the vibrational modes of molecules.  Other authors sometimes wish to reserve this notation for different purposes and Kimble (5), whose work should appear later in publication and was done concurrently with this investigation, will probably use the Greek letters (alpha, beta, etc.) for vibrational modes.  This is because he has an additional notation problem.]  The $A_u$ and the one $B_{1u}$ modes are both predicted to be infrared active from symmetry reasons although the $A_u$ mode will be active only in the condensed phases.  Additionally, the problem of certain other bands which appear in the infrared spectra, and which are apparently the result of decomposition products and combination bands, needs to be explained.  Now, if the low lying $A_u$ and $B_{1u}$ fundamentals, which Spencer, et al. (4) predicted should lie at about 550 to 350 $cm^{-1}$ and below 300 $cm^{-1}$ respectively, could be found then a normal coordinate analysis could be made on s-tetrazine (assuming Raman active modes were also found).  It could also be possible to make a complete vibronic analysis such as was attempted previously.

1.3     The Research Goals

Under the guidance of Professor G. H. Spencer, the author attempted to find the two low lying infrared fundamentals, determine the nature of the other previously unassigned bands and decomposition

products, and clear up other minor problems involved with s-tetrazine. (The Raman problem and a complete vibrational analysis was being done concurrently by Kimble (5) and, as was implied above, much information needed to be exchanged between him and the author.)  Since s-tetrazine was not available from any other source (only small quantities, a few grams at most, have ever been available to any worker in this field), sufficient amounts of the chemical had to be synthesized.  This was done by all three of us.  The synthesis, in quantities above 1 - 2 grams, is a project in itself of no small magnitude and was carried out basically as outlined in (4,6) and with some minor modifications (5).

## 2. INFRARED STUDIES AND THE $A_u$ AND $B_{1u}$ MODES

### 2.1 $A_u$ and $B_{1u}$ Mode Problems

The $A_u$ and $B_{1u}$ fundamental modes were predicted by Spencer, et al. (4) to lie between 550 - 350 $cm^{-1}$ and below 300 $cm^{-1}$, respectively. The problems that prevented their being observed are described by Spencer (6). They may be summarized as follows:

a. The s-tetrazine crystals can't be ground finely enough to make alkali halide salt pellets; the crystals have a waxiness that apparently prevents the making of a homogeneous salt pellet.

b. The pellets that were attempted (KBr, KI, and LiF) were, in addition to being nonhomogeneous, not transparent enough to take an infrared spectra.

c. A specific search was made for the $B_{1u}$ mode in a 10 cm gas cell with KI windows down to 295 $cm^{-1}$ with negative results.

d. No indications of either the $A_u$ or the $B_{1u}$ fundamentals could be found in solution or solid cold film spectra. As was noted previously, the $A_u$ mode is inactive in the gas phase from symmetry considerations (see any standard character table for symmetry point group $D_{2h}$) and hence cannot be observed in gas phase studies even down below 300 $cm^{-1}$.

### 2.2 Alkali Halide Pellet Techniques

The salt pellet problem was overcome by the rather simple expedient of not grinding the s-tetrazine crystals, but instead, by using a high speed vibrator mixing device. The procedure is as follows: All parts and the alkali halide powder used in making the pellets must be as dry as possible by heating in an oven to over 150 C for at least one hour. The metal capsule (and also the small

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metal weight which fits inside the capsule) which is used to hold the salt and sample mixture while on the vibrator is removed from the oven only a few minutes before the salt and sample are to be weighed. These items should have just cooled to room temperature at about the time the weighing is finished. They cool fairly rapidly. However, the salt to be used and the large pellet die must be removed from the oven much earlier and in sufficient time to allow them to cool to around room temperature prior to using either one of them. The idea behind this cooling procedure is to prevent the s-tetrazine from subliming upon contact with heated objects and yet to keep moisture to the minimum. The salt and s-tetrazine are weighed as rapidly as possible, then placed in the capsule with the weight, shaken on the vibrator for about 20 seconds, removed, the weight separated from the salt mixture, the mixture placed in the die immediately, and pressed on the hydraulic press under vacuum. It is apparently important to distribute the salt mixture evenly on the die to get a pellet that is transparent over the whole surface. S-tetrazine does not produce satisfactory pellets if too much of it is used or the mixture not as evenly distributed as is possible. Pressing times are more an art than anything else. During pressing it must be remembered that the s-tetrazine is being lost due to local heating in the press and that water vapor is being introduced through the edges of the die since the interior of the die is under vacuum. Further, the removal of water cannot be accomplished by any usual method, such as heating the pellet in or out of the die, since the vapor pressure of the s-tetrazine is close to that of the water. When a satisfactory pellet is obtained it is mounted in the usual manner on the spectrophotometer and the infrared spectrum taken.

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## 2.3 Observation of the $A_u$ and $B_{1u}$ Modes

Initially KBr was used in making pellets and a pure KBr pellet was made at the same time for use in the reference beam path as a compensator. The infrared spectra were taken on a Perkin - Elmer Model 621 Grating Spectrophotometer (see Appendix I for details of operating procedures). Figure 1 shows an infrared spectra obtained by these methods.
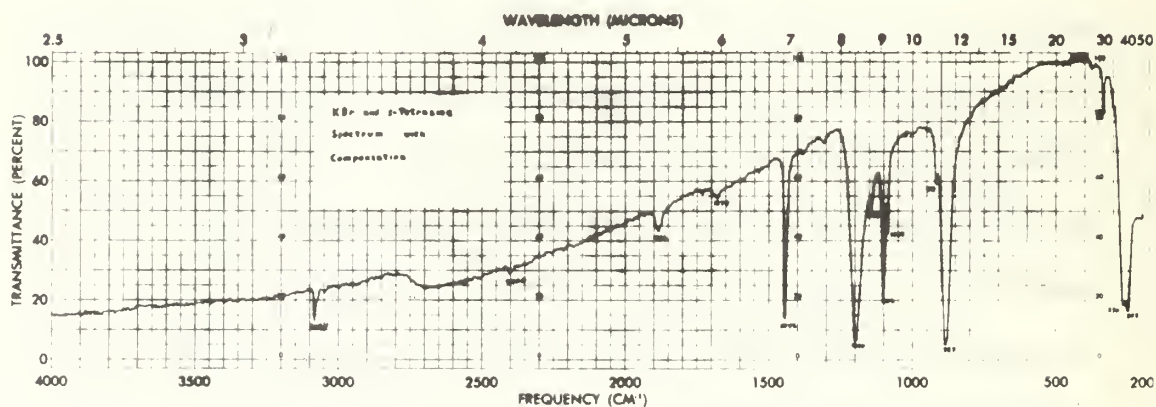


FIGURE 1.

The $B_{1u}$ fundamental mode appears at 252 cm$^{-1}$ although there is a second "peak" at 270 cm$^{-1}$ which we have not been able to resolve into a true doublet. In this regard, we also find similar behavior for most of the other strong peaks of s-tetrazine.

The $A_u$ fundamental mode appears at 337 cm$^{-1}$ and is of much less intensity than the $B_{1u}$ mode peak. This $A_u$ mode, which is inactive by symmetry in the gas phase, becomes allowed in condensed

phases by molecular interactions and, as predicted by Spencer, et al. (4,6), it "should not produce a very intense absorption band in the solid state spectrum." The $B_{1u}$ mode was predicted to be moderately intense, and, as we can see in Figure 1, this is confirmed.

Some other features of Figure 1 deserve comment. We find that our pellet spectra and the cold film spectra in reference (4) show very similar features both as to band frequencies and intensities. We feel that from this we can be fairly certain that both spectra represent true spectra of s-tetrazine with a minimum of contamination since each was prepared under much different conditions and it is rather unlikely that any impurities would be carried along equally well by both procedures.

Before we discuss the assignment of previously unassigned peaks we should note that some Raman frequencies have been obtained and kindly made available to the author by LCDR Kimble (5). All of them have not yet been determined but those which have, as well as some probable and possible ones, are listed in Table I along with the infrared active modes.

From this information it would appear that the 1142 $cm^{-1}$ [1147 $cm^{-1}$ in (4)] band which Professor Spencer did not assign as a fundamental band can now be explained as probably a combination band of the 337 $cm^{-1}$ $B_{1u}$ fundamental mode and the 798 $cm^{-1}$ gerade fundamental mode. The 1679 $cm^{-1}$ band (the 1697 $cm^{-1}$ band in (4) was likewise not assigned) can be explained as a combination band of the 252 $cm^{-1}$ $A_u$ mode and the 1412 $cm^{-1}$ gerade mode. The very weak 1075 $cm^{-1}$ band seen in (4) and which was not assigned at that time does not appear in our pellet spectra and this supports the

TABLE I

ASSIGNMENT OF FREQUENCIES

| Pellet Spectra | Cold Film Spectra from Spencer, et al. (4,6) | Raman Spectra from Kimble (5) | Assignments |
|---|---|---|---|
| 252 cm$^{-1}$ | (below 300 cm$^{-1}$) | --- | $B_{1u}$ |
| 337 | 550 - 350 | --- | $A_u$ |
| 887 | 890 | --- | $B_{1u}$ |
| 918 | 925 | --- | $B_{3u}$ |
| Not observed | 1075 (?) | --- | None |
| 1088 | 1090 | --- | $B_{2u}$ |
| 1102 | 1106 | --- | $B_{3u}$ |
| 1142 | 1147 | --- | Comb. Band |
| 1200 | 1200 | --- | $B_{2u}$ |
| 1310 (?) | Not observed | --- | None |
| 1442 | 1448 | --- | $B_{3u}$ |
| 1679 | 1697 | --- | Comb. Band |
| 1882 | 1898 | --- | Comb. Band |
| 2400 | Not observed | --- | Comb. Band |
| 3084 | 3070 | --- | $B_{2u}$ |
| --- | 737 | 737 cm$^{-1}$ | $A_g$ |
| --- | Freq. predicted for each mode in (4,6) are all approx. except for one which was obtained from vibronic analysis | 3088 | $A_g$ |
| --- | | 798 | Following are all gerade with no mode assignments as yet available |
| --- | | 1017 | |
| --- | | 1302 | |
| --- | | 1412 | |
| --- | | 1519 | |
| --- | | 460 (?) | |
| --- | | 1278 (?) | |

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previous nonassignment. We have observed a 2400 cm$^{-1}$ band which was
not previously reported and this probably is a combination band of the
1102 cm$^{-1}$ B$_{3u}$ fundamental mode with the 1302 cm$^{-1}$ gerade mode. The
1882 cm$^{-1}$ band [1898 cm$^{-1}$ in (4)] is possibly a combination band of
the 1088 cm$^{-1}$ B$_{2u}$ mode and the 798 cm$^{-1}$ gerade mode although combina-
tions such as the 887 cm$^{-1}$ B$_{1u}$ mode and the 1017 cm$^{-1}$ gerade mode
are also possible. There are only a very few remaining features on
our spectra and they may be due to noise, unbalancing of the elec-
tronics in the instrument, or weak combination bands, but we shall
not attempt to analyze such small features.

Results similar to those obtained from the KBr pellets were
obtained from the CsBr pellets again using a compensating pellet of
pure CsBr (see Figure 2). There was some difficulty in obtaining
transparent pellets of CsBr and s-tetrazine. The only spectral
features which differ from the KBr data are the small peak at 630 cm$^{-1}$
which was absent (or lost in noise) in the KBr runs and the lack of a
significant peak at 1679 in the CsBr runs (again, it may be lost in
the noise that we see in that region of the CsBr spectra). This loss
of a peak in CsBr doesn't bother us too much since the pellet is not
very transparent there and any small absorption band could get lost.
The 630 cm$^{-1}$ band occurs at a place where there is an interchange in
the instrument and it may be nothing more than an artifact; otherwise,
we will have to await further low frequency Raman mode information
before we can say if it is a combination band.

One thing that has hindered us in this work is that we were
not able to make more concentrated salt s-tetrazine mixtures to bring
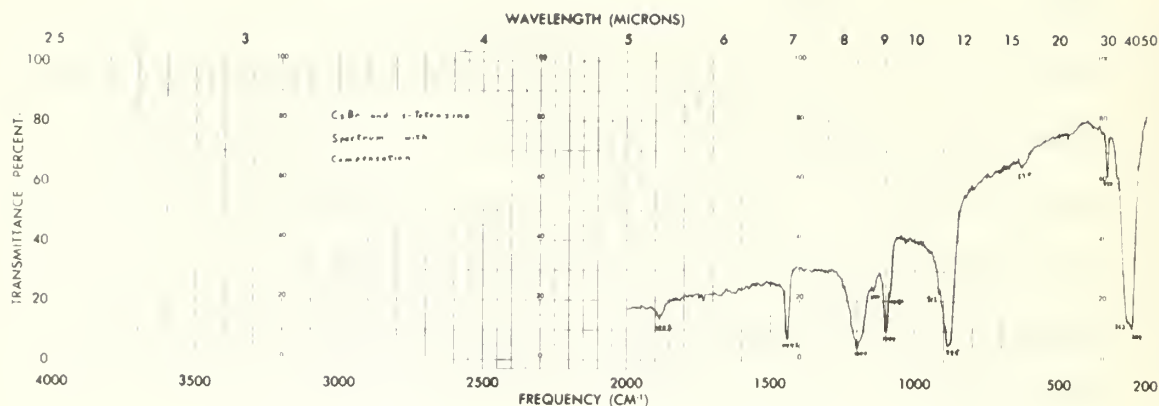out these weak bands more strongly; for, as can be seen in the

FIGURE 2.

spectra, even some of the moderate concentrations give pellets which are transparent only below about 1500 $cm^{-1}$. The problem is alleviated somewhat by use of the compensating pellet although resolution suffers especially at the low frequency end of the spectra. This is due to the additional slit widths required for the lowered energy. Without the use of a double beam instrument, it would be extremely difficult to see the low lying $B_{1u}$ mode, particularly with KBr. Figure 3 shows that this mode lies on the KBr cutoff region and its detection can easily be overlooked.
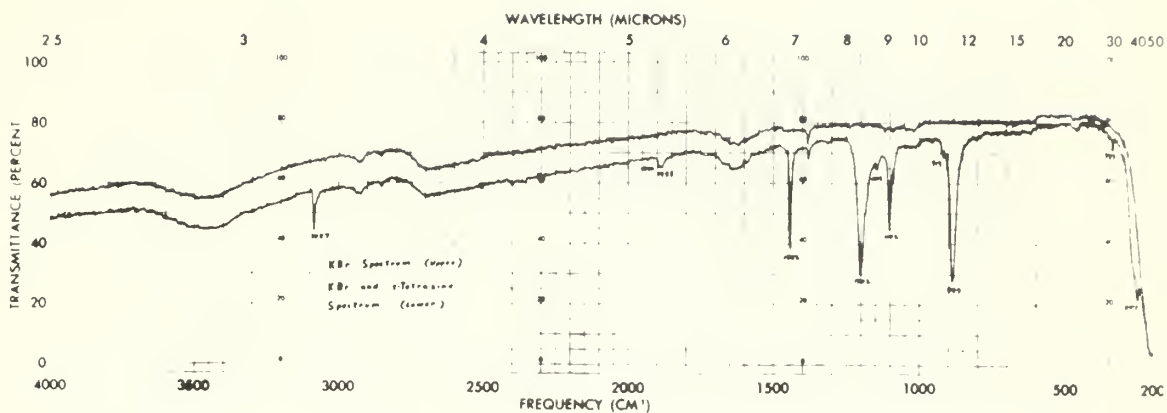
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FIGURE 3.

## 2.4 Near Infrared Region Studies

The spectra of s-tetrazine in the NIR region was taken on a Beckman DK-1A Spectrophotometer (see Appendix II). The solubility of s-tetrazine is not great enough in the solvents which we tried to give enough bands which could be used to find any new low lying infrared or Raman active modes in this combination band region. Those bands that we were able to observe, however, were in good agreement with the expected positions of combination bands as described by Kaye (14,15).

# 3. DECOMPOSITION STUDIES ON s-TETRAZINE

## 3.1 Solution Phase Thermal Decomposition

$CCl_4$ solutions of s-tetrazine (approximately saturated) were prepared, aliquots placed in stoppered 1 cm Beckman quartz spectrophotometer cells and then placed in small metal desiccators (along with the other cell of the matched pair) which were sealed with masking tape. The other cells of the matched pairs were filled with pure $CCl_4$. The desiccators were used to prevent moisture from condensing on the cells when removed from the refrigerator and to keep all light out of the solutions. One set of cells was kept at 2 C, the second set at 23 C, the third set at 57 C (with small temperature variations of 4 C downwards when the oven door was opened for other purposes), and a fourth set, also at 23 C, but with their stoppers removed to allow air to reach the solutions. The visible spectra was taken with each set of cells at various intervals, ranging from a few hours, initially, to two and more days, later in the experiment. A Beckman DK-1A dual beam NIR-VIS-UV spectrophotometer was used for this purpose (see Appendix II for details of operating procedures). The cells were allowed to reach room temperature, of course, prior to the taking of their spectra. The open cell experiment was useful for only a day as the $CCl_4$ evaporated too rapidly to yield any significant results. We expected this but we thought that if oxygen played a major role in the decomposition that it would show up this fact in a few hours and point the way for future experiments with both oxygen and inert gas environments. The open cell did not show any decrease in s-tetrazine absorbance and, in fact, showed some

increase as the $CCl_4$ evaporated slightly more rapidly than the
s-tetrazine was lost through evaporation.  Eventually the cells which
were kept at 57 C showed significant volume loss and this caused the
experiment to be terminated at 310 hours after starting.

During the experiment no changes in either the absorbance or
the spectral details could be observed in any of the sets of cells.
We must conclude that s-tetrazine solutions ($CCl_4$) do not thermally
decompose to any measurable extent over many days.  This was somewhat
surprising at first since we had noticed that other s-tetrazine solu-
tions of $CCl_4$ would lose their absorbance, although they were not kept
under controlled conditions.  Up to this time we had been careful,
however, to store all s-tetrazine solutions in a refrigerator.  Ap-
parently this is an unnecessary precaution, at least for solutions
that are to be used within a week or two.

## 3.2  Solution Phase Photodecomposition

$CCl_4$ solutions of s-tetrazine were prepared as for the thermal
decomposition studies above and for the initial experiments were
placed in 1 cm Beckman quartz cells designed for far UV work and
exposed to a small mercury lamp at distance of 20 cm.  The spectra
were taken at various intervals, again on the DK-1A.

The results are shown in Figure 4, which is a plot of
absorbance using a log scale versus time on a linear scale.  It is
apparent that the slope of the line through the data points is
straight over an interval of almost two orders of magnitude of
absorbance (over 5 'half lives' of s-tetrazine for this experimental
arrangement).  It is therefore fairly obvious that we are witnessing
a photochemical reaction involving the decomposition of s-tetrazine.

We obtained the same results using cyclohexane solutions of s-tetrazine. Incidentally, we checked for possible heating of the solution by the mercury lamp and found none, which reinforced our findings above with respect to thermal decomposition.
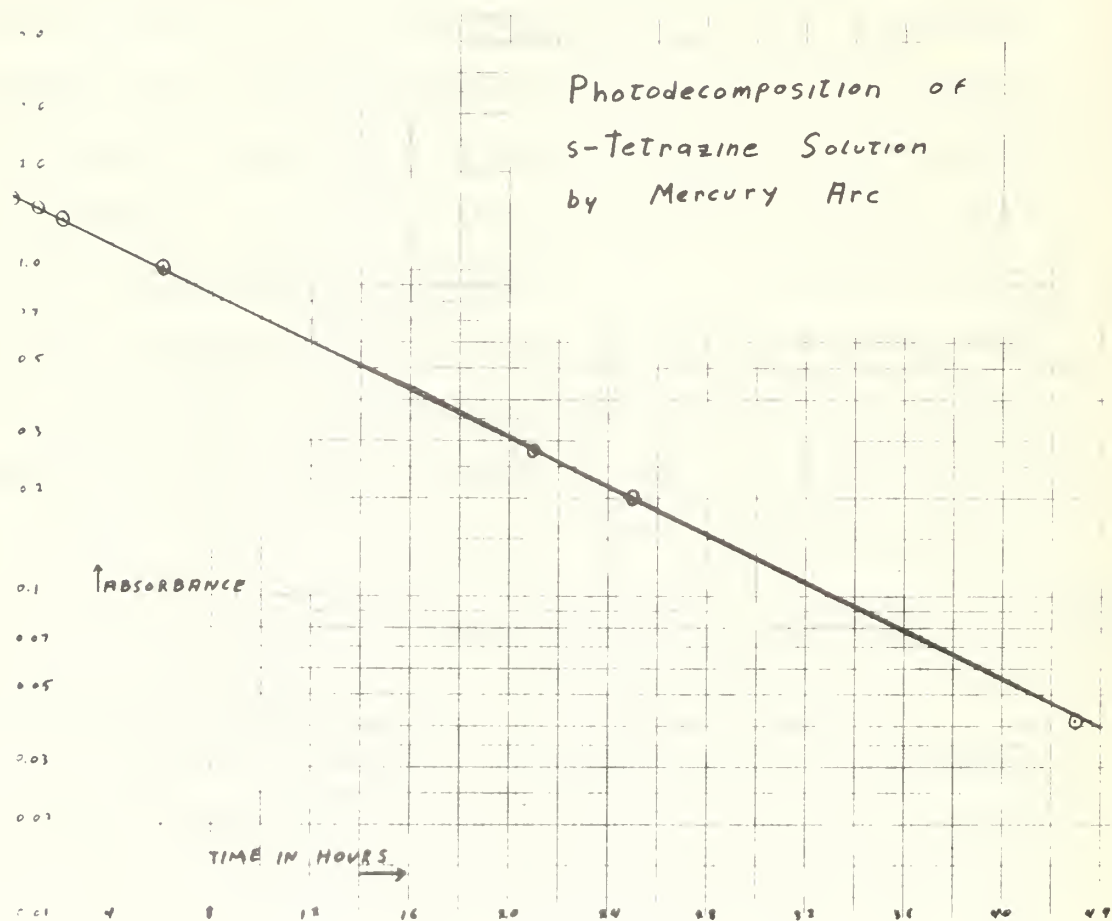


FIGURE 4.

A note about the mercury lamp should be made here. The lamp used in this first portion of the photodecomposition studies was small and of the ordinary student type found in optics courses with prism spectroscopes. It did not have a special quartz lens to transmit the far UV as more sophisticated models have.

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It then became apparent that any 'bleaching' of the s-tetrazine solutions we experienced was due to this photodecomposition. Hence, for storage of s-tetrazine solutions it is most important to make sure they are protected from light rather than heat, particularly from sunlight and fluorescent light.

Next we attempted to determine the photodecomposition as a function of the wavelength of the incident light. A grating monochromator was used with a 250 watt quartz tube mercury arc lamp to isolate the 2537 A, 3132 A and the 4358 A lines of mercury. The use of the monochromator, as opposed to filters, was required as will be apparent from section 4.2 below. For the time being it is sufficient to say that even 0.1% stray light from one of other of the three lines of mercury listed above would invalidate this set of experiments. Consequently, filters were undesirable since they are generally fairly broad in band width.

The monochromator had certain undesirable features associated with it, the primary one being that the size of the exit beam of light was not large enough to fill the area of the face of the cell holding the solutions. This meant that not all of the solution was being irradiated and precise quantitative results could not be obtained. In the experiment we used 1 mm quartz cells designed for far UV work and designed a cell holder that allowed the cells to be removed from, and replaced in, the holder at exactly the same position with respect to the monochromator exit slit.

Using $CCl_4$ solutions of s-tetrazine it was found that with the 2537 A line the absorbance dropped from .45 to less than .04 in 4 hours. Using the 3132 A line it was found that the absorbance dropped

from .45 to .22 in 144 hours. When we used the 4358 A line there was no significant change in the absorbance over a 72 hour period. Of course, all experiments were carried out with the cells protected from stray light by a heavy black felt cloth.

If one is willing to accept the values of relative line intensities of mercury arcs from the Handbook of Chemistry and Physics (7) (the data contained therein being obtained from the M.I.T. Wavelength Tables) and we further assume that the mono-chromator light losses are approximately equal (say less than 50% differences for the three wavelengths used), then we arrive at the approximate relative intensities of incident light upon the cells as: 2000 for 2537 A, 600 for 3132 A, and 3000 for 4358 A (or almost a ratio of 5:2:13 for number of incident quanta). This leads us to the conclusion that photodecomposition is taking place at 2737 A, is not taking place for 4358 A (to any appreciable extent), and that at 3132 A we are observing much less photodecomposition than at 2537 A (lower quantum yield). We reached these conclusions from the estimated ratio of the 2537 A to 3132 A intensities (or more strictly, incident quanta) coupled with our observation that the ratio of the rate of absorbance changes is at least two orders of magnitude greater for the 2537 A incident light than for the 3132 A light. We used for the intensity of the 3132 A line the sum of the two lines actually listed in (7). They are 400 for the 3131.55 A and 200 for the 3131.83 A. The characteristics of our monochromator, combined with the relatively wide slit widths we used, made us certain we were not resolving these two lines and that their sum should be used in our calculations.

The calibration of the monochromator was done by a rather simple method in the UV region. We used anthracene crystals held in front of the exit slit and checked to see that the indicated wavelengths (indicated on the wavelength counter dial) corresponded to the maximum fluorescence of the anthracene crystal in that particular wavelength region. The visible region was checked simply by looking through the exit slit and locating the visible mercury lines.

These conclusions of ours are in agreement with the absorption spectra data, that is, we shouldn't see photodecomposition in a region that doesn't absorb. Spencer, et al. (1) report a broad peak in the vapor phase at 2470 A extending from 2800 A to approximately 2200 A and which encompasses the 2537 A line we used in our work. Mason (3) reports a broad shoulder on the same peak as above which is centered around 3200 A. Mason's work was carried out in solution when he reported this shoulder and he indicates that the shoulder has an extinction coefficient of approximately two orders of magnitude less than the main peak. We also found (Section 4.2) that there is absorption in the 3132 A region so our rough quantitative results are at least reasonable with the other known information.

For future solution phase photodecomposition work the actinometric procedures developed by Parker and co-workers (8,9,10) using potassium ferrioxalate might prove to be very useful. Certainly, if precise quantitative data on quantum yields is desired, then some sort of actinometer must be employed. We attempted to use uranyl oxalate for this purpose but it just is not sensitive enough to the amount of light coming from the monochromator.

Attempts to obtain the infrared spectra of s-tetrazine photodecomposition products in solutions such as Nujol and $CCl_4$, and in solid films on salt plates, all failed to give any results. Our solution spectra showed only the solvent and no other bands were detectable. The solid film experiments were attempted by spreading s-tetrazine crystals over the face of the salt plate, the salt plate placed in an evacuated container, and the irradiation from a mercury arc done through the glass walls of the container. The same experiment was repeated using nitrogen in the container. Both of these experiments gave a salt plate which was covered with brown oily spots but the spectra showed no peaks; only an overall reduction of light intensity in the sample beam.

3.3  Gas Phase Decomposition Studies

The gas phase studies were made on the Perkin - Elmer 621 spectrophotometer and used a 10 cm gas cell designed by us with KBr windows and which was wrapped with a heating tape. The windows were sealed on the cell with Glyptal and it should be mentioned that only a thin strip of Glyptal should be used on the ends of the 40 mm glass tubing which comprises the cell body. If more is used then leaks are almost certain to be present and painting more Glyptal on in an attempt to close the leak only makes the removal of the 55 mm KBr windows more difficult later and rarely seals the original leak. The cell had a 'finger' attached to the bottom of it that could be immersed in an ice bath or liquid nitrogen to collect s-tetrazine when it was introduced into the cell in vapor form while under vacuum. Both conventional, all-glass stopcocks designed for high vacuum work and Teflon stopcocks with rubber 'O' rings were used in

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making the cells. The Teflon stopcocks appeared to hold a vacuum somewhat longer but after high temperature runs of around 120 - 130 C the rubber 'O' rings failed and the entire stopcock had to be replaced using up a fair amount of glassblowing time. The s-tetrazine was introduced into the cells through a high vacuum system and the cooled crystals, as well as the entire cell, were pumped down separately to approximately .001 mm of Hg.

Initially, the crystals were triply sublimed back and forth through a small portion of the vacuum system with pumping down between sublimations and with the third sublimation being into the gas cell. However, single sublimations seemed to be just as adequate and in subsequent work we used only single sublimations.

When sufficient crystals were introduced in the cell it was closed off and a room temperature run was made followed by the higher temperature runs at correspondingly greater pressures of s-tetrazine. The temperatures were measured by inserting a thermometer between the heating tape and the gas cell wall. This gave only approximate values, but from the fact that the runs were at readings of near 120 C on the thermometer and the fact that the crystals could be made to completely vaporize, we estimate the temperature to be at least 100 C. The cell was protected from light during these runs to the maximum possible extent. It did receive some light during the movement of the cell from the vacuum system to the spectrophotometer and also to and from the desiccator in which it was stored between runs. A series of runs was made with one sample in the cell over a period of a week. The cells held a vacuum of better than 0.1 mm of Hg for a few days and consequently the leakage of air into the cells cannot be discounted in trying to interpret the final results.

One observation that was very apparent to us was that the band centered at 711 cm$^{-1}$ was present in all s-tetrazine vapor spectra and at higher concentrations of this material there was a very definite rotational structure on both sides of the main (and very sharp) band. Spencer, et al. (4), reported this band to be HCN from its frequency [712 cm$^{-1}$ in (4)] and since we have observed the typical P, Q, R branch structure associated with molecules of this type we can state with much confidence that it is HCN (see Figure 5). It behaves in a strange way in our studies, though. It did not increase and decrease in a manner consistent with its being a simple end decomposition product. It would appear in fresh s-tetrazine vapors at room temperature, as it did in Figure 5, as a very intense band and other times it would be almost absent even from samples prepared under the same conditions (to the best of our knowledge). It would not increase in a definite manner with time or upon heating. And the most surprising thing was that it would decrease sometimes upon cooling! Now, HCN has a boiling point of 26 C at 760 mm of Hg and cooling the gas cell from around 100 C to around 40 C should still leave all the HCN in the vapor phase. In fact, considering
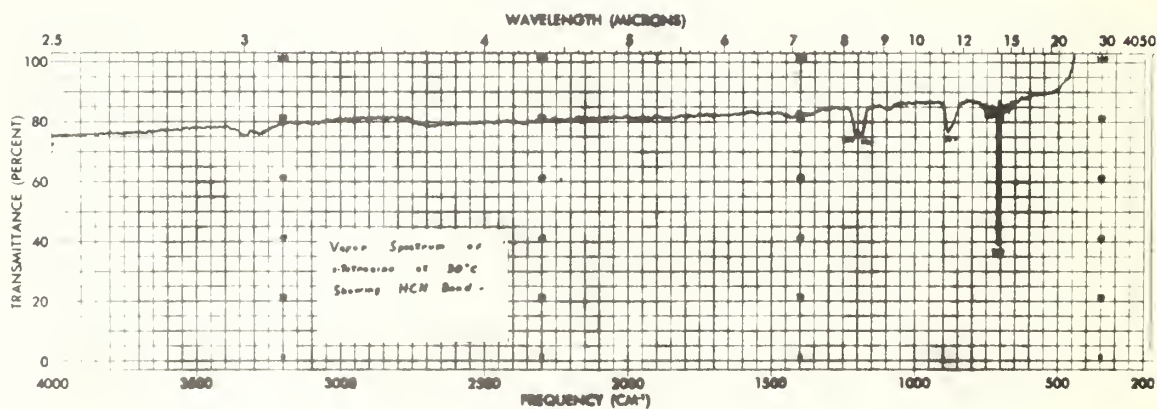
FIGURE 5.

the amounts of it probably present, it should be in the vapor phase
at all times.  That it is a probably decomposition product is not in
doubt but it apparently is removed by some process we do not under-
stand as yet.  Possibly the slight but slow leakage of air into the
cell has something to do with it.

From Figures 6, 7 and 8 we can get a picture of how the gas
phase spectrum changes with time and successive heating each day.
Figure 6 shows the fresh s-tetrazine vapor upon heating to over
100 C.  The distinctive water bands can be seen as being present
in the reference path.  Of the two cells used in any run, the one
that held a vacuum the best was always used for the sample.  In
this case the sample cell had been evacuated the day before.



FIGURE 6.

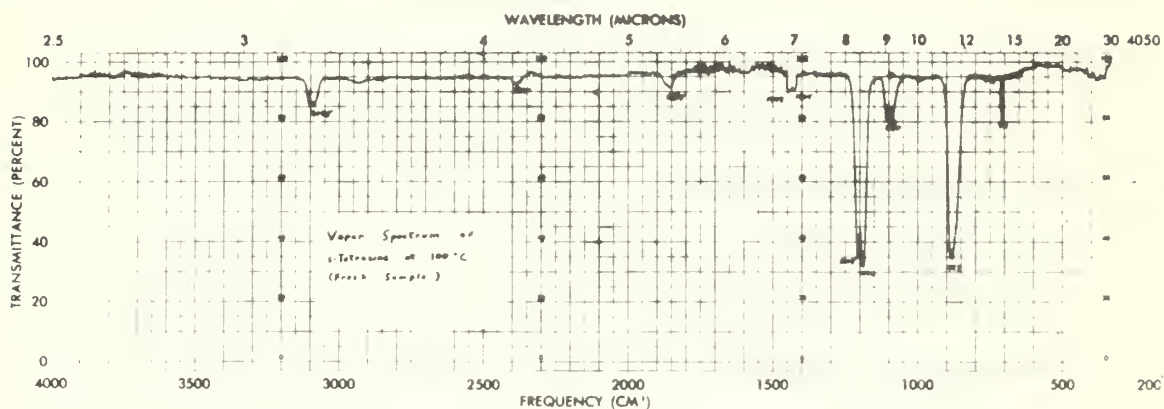A simple test for leakage was available to determine if the
sample cell had leaked, though.  The reference cell was pumped down
and the spectra run.  If the sample cell had leaked we should see
the water and/or the $CO_2$ bands appearing as normal absorption bands
in the spectra.  Of course, in the case of the reference cell leaking
the absorption bands due to these two species appear reversed and

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point toward the top of the spectra as they do in Figure 6. It is

no problem to re-evacuate the reference cell and continue to use it.

We made it a practice to check the cells as shown in Figure 6 each

day and then evacuate the reference cell and proceed to make our

normal runs. This insured any leaks would show up if they did

occur. Figure 7 shows the same sample after five days.
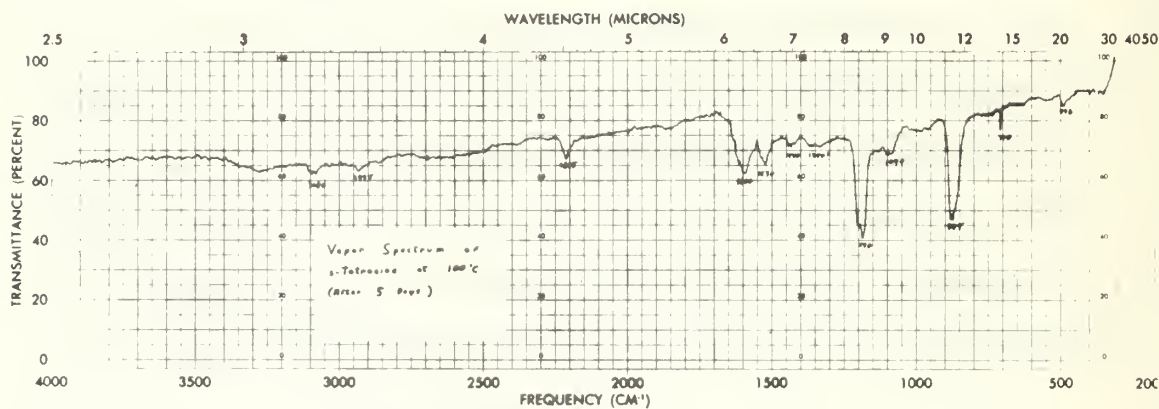


FIGURE 7.

We cannot tell whether the peaks which have built up are due

to gases or solid products. (The build-up of the peaks can be seen

to be gradual with each day but only the five-day results are neces-

sary for our purposes here.) Figure 8 shows the same cell but which

has been pumped down for 18 hours to remove the vapors so as to

determine which peaks were due to solids and which due to gases.

The most intense lines of s-tetrazine remain although they are

reduced to about the same peak height as room temperature vapor phase

spectra show. The only explanation we have for their remaining is

that they are the result of s-tetrazine molecules 'trapped' with the

decomposition products which are solids. All of these peaks can be

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removed by one washing of the windows with acetone, the only other change
being that the windows are then even less transparent than before washing.

WAVELENGTH (MICRONS)
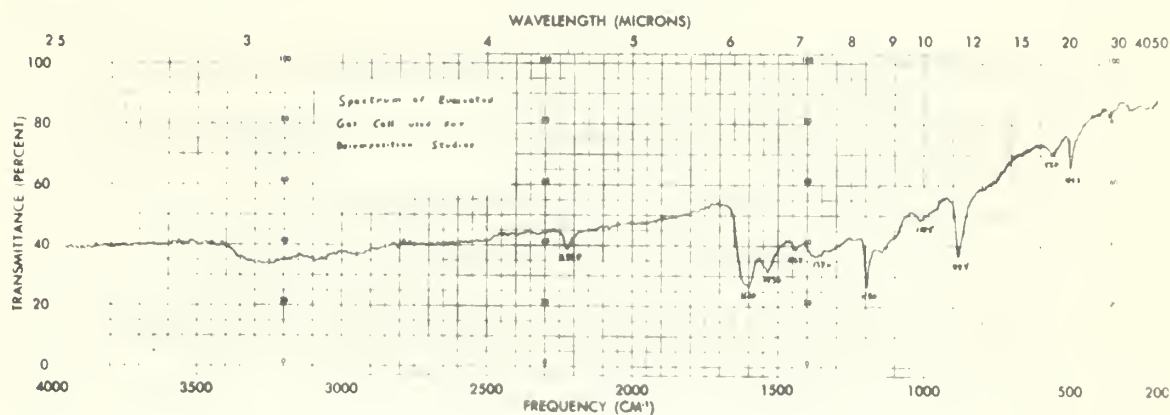
FIGURE 8.

This indicates to us that the last remaining s-tetrazine and the solid
decomposition products are removed together. It is interesting that
all the decomposition products (except HCN) that we can observe are
solid. Of course, some additional products could be gases that we
could not see in the infrared because of symmetry considerations or
because they do not have sufficiently large extinction coefficients
or concentrations in our cell. These solid products had a brownish
color that we could see faintly on the cell windows. This same
color is present when s-tetrazine crystals decompose in the air.
It is only in solution phase decomposition that we do not see this
brown color of certain decomposition products. The solutions we
studied all went from red to colorless (being clear all the time).

From the frequencies of these product bands it has not yet been possible to characterize the compounds other than in a general way. In Table II we have listed some of the possible assignments to the product bands although some of these are little more than suggestions for future work. The two bands listed in (4) as being ones that increased with time and therefore likely decomposition products ($1758$ cm$^{-1}$ and $2930$ cm$^{-1}$) are still unaccounted for. The $1758$ cm$^{-1}$ band was not observed by us in these studies. The closest we have been able to come to an explanation of the $2930$ cm$^{-1}$ band is that it could be a hydrocarbon impurity possibly on the cell windows. The other bands are listed in Table II along with the above mentioned assignments.

TABLE II

Decomposition Product Frequencies and Assignments

| Frequency | Assignment |
|---|---|
| $2220$ cm$^{-1}$ | solid product - probably $C \equiv N$ str |
| 1600 | solid product - possibly $N = N$ or $C = N$ str |
| 1530 | solid product - possibly $N - H$ bend |
| 1370 | solid product - possibly $C - H$ bend |
| 1005 | solid product - possibly $C - N$ str |
| 711 | gas product   - HCN |
| 492 | solid product - probably $C - C$ bend |

Attempts to obtain the photodecomposition products spectra did not give very much information. We found small peaks at 2220, 1600, 1520 and possibly $1680$ cm$^{-1}$. Again the HCN peak at $711$ cm$^{-1}$ was absent from the final spectra. The peaks were very small and quite

broad.  We again saw the same brown oily film produced as in the solid film experiment.  It was formed primarily around the cold finger, over the s-tetrazine crystals, up in the neck of the cell near the stopcock, and on those parts of the cell body nearest the mercury lamp.

We used a different mercury lamp for this experiment.  It was a small pen sized lamp with a metal cap over the quartz tube and with a small slot cut in the cap to give a fairly good directional effect. The sample chamber in the infrared spectrophotometer is only about 15 cm wide and about 15 cm deep, and in such cramped spaces we obviously could not use the large 250 watt mercury arc setup.  The lack of photodecomposition product band intensity in this experiment can probably be attributed to the fact that we were working at room temperature (to keep thermal decomposition from occurring), and the s-tetrazine crystals themselves were covered with this brown oily substance which may have further reduced the amount of vapor formed in the cell.

# 4. VISIBLE-ULTRAVIOLET SPECTRAL STUDIES

## 4.1 Determination of Extinction Coefficients

In the past only very limited quantities of s-tetrazine were available, vapor pressure measurements were difficult at best, and, consequently, not much work was done in determining the extinction coefficients of the $n \rightarrow \pi^*$ or the $\pi \rightarrow \pi^*$ transitions. Spencer, et al. (1), estimated the vapor pressure to be about 1 mm of Hg in one of their experiments and arrived at a value of roughly 3700 for the extinction coefficients at 2470 A (in the $\pi \rightarrow \pi^*$ region) in the vapor phase. (Extinction coefficients reported in this work all have the usual units of liter/mole-cm). Mason (3) shows electronic spectra of s-tetrazine in cyclohexane and in water. The figure in his paper measures 2½ by 2½ inches, covers the spectrum from 45,000 to 15,000 $cm^{-1}$ and has a log scale of the extinction coefficients of over three magnitudes. He further makes no reference to any values of the extinction coefficients in his series of papers (3). Consequently, we are in doubt as to what his values really are. We estimate them from his chart to be about 3000 ± 1000 for the $\pi \rightarrow \pi^*$ region and about 700 ± 200 for the $n \rightarrow \pi^*$ region, both being from his cyclohexane solution work. He also shows a shoulder on the $\pi \rightarrow \pi^*$ band which he attributes to a second $n \rightarrow \pi^*$ absorption around 3200 A (30,000 $cm^{-1}$) and which appears to have an extinction coefficient of around 20, again this being in cyclohexane.

Our present work agrees with both of these sources but we do feel that our values are somewhat more precise than Mason's. The extinction coefficients are listed in Table III. All work was done on a Beckman DK-2A spectrophotometer (see Appendix II)

## TABLE III

### EXTINCTION COEFFICIENTS OF s-TETRAZINE

| Wavelength | $\varepsilon$ in $C_6H_{12}$ | $\varepsilon$ in $C_6H_6$ |
|---|---|---|
| 5800 A | 38 l/mole-cm | --- |
| 5580 | 870 | 590 |
| 5370 | 1300 | 900 |
| 5160 | 890 | 730 |
| 4980 | 490 | 430 |
| 4810 | 220 | --- |
| 2470 | 2900 | --- |

(Note: The $C_6H_6$ spectra have less detail and some bands are not present as separate bands but appear as shoulders or are absent. $C_6H_6$ itself absorbs in the ultraviolet region and the $\varepsilon$ at 2470 A in this solution cannot be measured.)

The values listed in Table III are accurate to within 10 percent. We feel that they probably are accurate to 5 percent and we estimate our weighing error to be no larger than this amount. This error arises because s-tetrazine sublimes at room temperature. Our weighing procedure was to first get an approximate weight of one single, large crystal, set the balance to a weight a little less than the rough weight, watch the weight of the crystal approach this set value, as soon as it did so, to remove the crystal with tweezers and place it in a volumeteric flask partially filled with the appropriate solvent; and then, when the crystal completely dissolved, make the solution up to the required volume, the crystals, of course, being protected from light as much as possible.

4.2  Solvent Shifts and n → $\pi^*$ and $\pi$ → $\pi^*$ Bands.

Table IV shows the results of our studies for the n → $\pi^*$ band, as well as others, in solvent shift work, this solvent shift work being the usual method of characterizing these two different types of transitions (12).

TABLE IV

SOLVENT SHIFTS FOR s-TETRAZINE

| Solvent | Our Values | Spencer (6) | Mason (3) |
|---------|------------|-------------|-----------|
| $C_6H_{12}$ | 5385 A | ≈ 5400 A | 5387 A |
| Vapor Phase | ---- | 5326 | ---- |
| $H_2O$ | 5060 | ≈ 5150 | 5102 |
| EtOH | 5330 | ≈ 5350 | ---- |
| $C_6H_6$ | 5350 | ---- | ---- |
| $CS_2$ | 5390 | ---- | ---- |
| $CCl_4$ | 5350 | ---- | ---- |

(Note:  The values from (6) are taken off of spectra contained therein and are only approximate.)

It is fairly evident from the above Table IV that in going from the non-polar solvents to the polar ones the characteristic blue shift is observed.  It should be noted that the spectra of s-tetrazine solutions in water are almost completely devoid of the usual sharp bands we find in the other solvents.  This makes it difficult to locate the exact shift that has taken place since we can no longer follow the location of the one most strongly absorbing band.

The $\pi$ → $\pi^*$ band shows the less well defined red shift in going from non-polar to polar solvents.  Our work shows that the absorption

maxima shifts from 2520 A in $C_6H_{12}$, to 2530 A in EtOH, and to 2550 A in $H_2O$.

Mason (3) reports that the shoulder he sees on the $\pi \to \pi^*$ band exhibits a solvent shift from 3200 A in $C_6H_{12}$ to 3050 A in $H_2O$. We do not see this as a distinct shoulder in our results but rather as a region where the absorption does not return to zero when scanning the spectrum from the visible through the ultraviolet regions. It looks to us more like a plateau which gradually rises until the $\pi \to \pi^*$ band is reached. We attempted to characterize this 'band' by solvent shift work but had no success. One experimental difficulty in working in this region is that of light sources and detectors. One must change light sources when leaving the visible region which uses tungsten lamps, and turn to hydrogen lamps, and then, either change photomultipliers or change the gain on one that can be used in both regions. More work needs to be done before this band can be considered as being fully characterized.

## 4.3 Fluorescence Studies

We attempted to obtain the fluorescence spectra of s-tetrazine but had no success. The Beckman DK-1A is not the instrument of choice in this type of work, however, and the fluorescence spectra of the compound has been obtained by others (13) using considerably better experimental equipment.

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APPENDIX I

Infrared Spectrophotometer Procedures

The Perkin-Elmer Model 621 Spectrophotometer is a dual beam, grating instrument which was used for our infrared studies from $4000\ cm^{-1}$ down to $200\ cm^{-1}$. Typical of our runs was to set the slit program setting to 1000, the gain to 5, attenuator to 1100, scan times were usually 20 minutes for the full range, the suppression to 7, the source intensity to 0.7 amperes, and the scale was always set at 1X (normal - no expansion).

Typical pellets were made from 1 - 3 milligrams of s-tetrazine with about 0.3 grams of KBr. Similar proportions were used for CsBr. The instrument was purged with dry air and water bands were not a problem with pellets except for that water which was incorporated into the pellet. Water bands did become somewhat of a problem when using the gas cells since the cover to the sample compartment could not be closed due to the size of the cells and the other equipment required to make the run. If the scan time was kept to at least 20 minutes this problem was overcome. The gas cells took up most of the light path length in the sample compartment, the purge operated continuously, and not too much water could get in the light path and what did was generally balanced out by the reference path if the scan time as mentioned before was kept at 20 minutes or longer. The instrument did have a tendency to jump to a new baseline as it went through the interchanges at around $2500\ cm^{-1}$ and again at around $600\ cm^{-1}$. These effects were deleted from the spectra shown in this work but in all other respects they are reproduced as faithfully as possible.

Visible - Ultraviolet Spectrophotometer Procedures

The Beckman DK-1A Spectrophotometer with the purge attachment and
other modifications for use in the far UV regions was used for the
near infrared, visible and ultraviolet studies. Its range was from
4000 mu to 190 mu (2500 $cm^{-1}$ to 52,630 $cm^{-1}$). Intermediate scan times
were used and typically a NIR-VIS study was made as follows: the
source was a tungsten lamp, lead sulfide detector was used, chart
speed was 1.0 cm per minute, wavelength drive was set to 10, the
time constant (period) was 0.1 second, the gain set on 12 except at
the low energy end of the NIR at which it was usually increased to
50, and the 0 - 100 percent transmission mode was used.

The instrument was designed for purge with an inert gas for
far UV studies but, contrary to the information in the instruction
book for the instrument, we found the purge should also be used when
working in certain regions in the infrared. The water bands there,
while not as bothersome as those in the fundamental region, were still
present. Since the lead sulfide detector is not as sensitive and the
energy emitted by the tungsten lamp through the glass envelope in
this region is low, any energy loss due to water (or anything else)
is undesirable since it forces the instrument to open the slits even
more and causes additional loss of resolution.

The instrument was slightly modified by us to incorporate the
feature described below. A remote switch box was made which could
be operated by someone standing at the spectrometer itself rather
than from the strip chart recorder. The switches placed on this
remote switch box included the one which controlled the chart paper

drive motor and the one which controlled the wavelength drive motor. The purpose of this modification made it possible to align the pen on a line on the chart paper with the wavelength indicator scroll in the monochromator housing. First, the chart paper drive is turned on until the pen just rests on a line on the paper and then it is turned off. Next, the wavelength drive is turned on and, at the instant the desired wavelength marking passes under the double hairline, the chart drive motor turned back on. The reason this is necessary is that the two motors are matched. But the chart paper moves at a much faster speed than the wavelength scroll. This means that the gears in the wave-length drive unit cause a fair amount of backlash to occur there while the backlash in the chart drive motor is only very slight. By operating the instrument in this manner it is possible to get exact correlation between the monochrometer indicated wavelength and the lines on the chart paper. Without it, it takes two people to accurately calibrate the chart paper. It also makes reading the spectrum much easier since the lines on the paper correspond to exact incremental wavelengths and not some odd reading like 543.45 mu.

The final comment about the DK-1A instrument which should be made is that the lamp housing needs to be redesigned. It is a time consuming job to change the lamp housing when running fluorescence studies. In this same connection the instruction book is wrong (it was written for the old single-source lamp housing) when it describes the method of lamp house removal and replacement. This comment has been passed on to the Beckman representative by the author.

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13. ABSTRACT

From earlier studies it was shown that neither a vibronic analysis nor a normal coordinate vibrational analysis of s-tetrazine could be done until two low lying, fundamental, vibrational modes ($A_u$ and $B_{1u}$) were found. This work reports on the discovery of these two modes, the assignments of various infrared absorption peaks based on them, and the problems surrounding their observation. They are located at 337 $cm^{-1}$ and 252 $cm^{-1}$ respectively. Since s-tetrazine had previously been reported to be metastable at room temperature, it was desirable to study its decomposition. Both thermal and photochemical decomposition work is reported and discussed. The extinction coefficients in various portions of the visible and ultraviolet regions have been determined, and observations concerning a possible second $n \rightarrow \pi^*$ electronic transition are reported.

| 14 KEY WORDS | LINK A | | LINK B | | LINK C | |
|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| s-Tetrazine | | | | | | |
| Infrared Spectra | | | | | | |
| Electronic Transitions | | | | | | |
| Fundamentals | | | | | | |
| Vibrational Modes | | | | | | |
| Thermal Decomposition | | | | | | |
| Photochemical Decomposition | | | | | | |
| Extinction Coefficients | | | | | | |
| Frequency Assignments | | | | | | |
| Salt Pellet Techniques | | | | | | |

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